

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 62-007745

(43)Date of publication of application : 14.01.1987

Jan. 14, 1987

(51)Int.Cl.

C08K 3/10

(21)Application number : 60-147305

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(22)Date of filing : 03.07.1985

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(54) WATER-ABSORPTIVE RESIN COMPOSITION ITS PRODUCTION AND WATER-ABSORPTIVE AND RETENTIVE AGENT

(57)Abstract:

PURPOSE: To obtain the titled composition of high water-absorption rate, good stability to moisture, high stability with time, etc., suitable for water retentivity enhancer for paper diaper and soil, by application of multivalent metal salt and/or hydroxide-contg. water on specific water-insoluble hydrophilic polymer granules.

CONSTITUTION: A water-insoluble hydrophilic polymer prepared by polymerization between hydrophilic and/or water-soluble monomer(s) and polysaccharide and/or crosslinking agent followed by, if needed, hydrolysis (e.g., hydrolyzate from starch-acrylonitrile graft copolymer) is made into powdery resin granules with a water content $\leq 20\text{wt}\%$, size $5W5,000\mu$ and water-absorptive power $\geq 60\text{ml/g}$. Following that, multivalent metal salt and/or hydroxide (e.g., calcium chloride, calcium hydroxide)-contg. water is applied on the surface of said granules. The amount of the above aqueous liquid to be applied is such as to be $0.01W20\text{wt}\%$ based on said resin granules.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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**Japanese Unexamined Patent Publication No.
7745/1987 (Tokukaisho 62-7745)**

A. Relevance of the Above-identified Document

The following is an English translation of non-English language information that may be relevant to the issue of patentability of the claims of the present application.

B. Translation of the Document

1. TITLE OF THE INVENTION

WATER ABSORBENT RESIN COMPOSITION,
PRODUCTION METHOD THEREOF, AND WATER
ABSORBING AND WATER RETAINING AGENT

2. CLAIMS

1. A reformed water-insoluble water absorbent resin composition, obtained by adding, as an essential component, water containing polyvalent metal salt and/or hydroxide to water-insoluble hydrophilic polymer particles made of hydrophilic and/or water-soluble monomer.

2. The reformed water-insoluble water absorbent resin composition as set forth in claim 1, wherein an amount of the polyvalent metal salt and/or hydroxide ranges from 0.01 to 10 wt% with respect to an amount of the hydrophilic polymer particles.

3. The reformed water-insoluble water absorbent resin composition as set forth in claim 1 or 2, wherein the

water-insoluble hydrophilic polymer is a polymer selected from: a hydrolyzed starch-acrylnitril graft copolymer; a cellulose-acrylic acid graft copolymer and salt thereof; a polyacrylamide cross-linked with divinyl compound and partially hydrolyzed polyacrylamide; a cross-linked poval; a saponified vinylester-unsaturated carboxylic acid copolymer; cross-linked polyethyleneoxide; a cross-linked starch-acrylamide graft copolymer; and a cross-linked starch-acrylic acid graft copolymer and salt thereof.

4. The reformed water-insoluble water absorbent resin composition as set forth in any one of claims 1 to 3, wherein the water-insoluble hydrophilic polymer is a polymer obtained by copolymerizing a material (A) such as (a hydrophilic and/or water-insoluble monomer) and/or (monomer which is changed into hydrophilic and/or water-soluble monomer by hydrolysis) and polysaccharide (B); a copolymer obtained by copolymerizing the material (A) and a cross-linking agent (C); or the material (A), the polysaccharide (B), and the cross-linking agent (C) as essential components, and by carrying out hydrolysis as required.

5. A method for producing a water-insoluble water absorbent resin, said method comprising the steps of: making water-insoluble hydrophilic polymer, made of hydrophilic and/or water-soluble monomer, into powdery resin particles whose water content is 20 wt% or less; and

dispersing water, containing polyvalent metal salt and/or hydroxide, to 0.001 to 20 wt% of the powdery resin particles.

6. The method as set forth in claim 5, wherein the powdery resin particles are high water absorbent resin particles whose water absorbing power is 60 ml/g or more.

7. The method as set forth in claim 5 or 6, wherein an amount of the polyvalent metal salt and/or hydroxide ranges from 0.005 to 10 wt% with respect to an amount of the powdery resin particles.

8. A water absorbing and water retaining agent, comprising a reformed water-insoluble water absorbent resin composition, obtained by adding, as an essential component, water containing polyvalent metal salt and/or hydroxide to water-insoluble hydrophilic polymer particles made of hydrophilic and/or water-soluble monomer.

9. The water absorbing and water retaining agent as set forth in claim 8 being used for a water absorbing article.

10. The water absorbing and water retaining agent as set forth in claim 8 being used for a water absorbing article such as a disposable diaper, a sanitary napkin, a wound dressing, an incontinence pad, a paper and fiber product water absorbency improving agent, or a sweat-absorbency providing agent.

11. The water absorbing and water retaining agent as

set forth in claim 8 being used for an agroforestry/horticulture water retaining agent, an architectural water absorbing agent, a civil engineering/industrial dehydrating agent, a heavy metal absorbing agent, a polluted sludge coagulating agent or chemical, an aromatic controlling/releasing agent.

3. DETAIL DESCRIPTION OF THE INVENTION

[Industrial Applicability]

The present invention relates to a water absorbent resin composition, a production method thereof, and a water retaining agent.

[PRIOR ART]

Recently, it has become general to use, in a sanitary napkin, a disposable diaper, or the like, a water absorbing material, having a relatively high water absorbing ability, such as cross-linked polyethyleneoxide, cross-linked poval, hydrolyzed starch-polyacrylnitril graft polymer, self-cross-linking polyacrylic acid metal, and the like. However, although each of these materials has high water absorbing ability, it is not sufficient as a material for a sanitary product or a disposable diaper which requires high water absorbing rate. That is, as the water absorbing ability is higher, the affinity with respect to water is higher. Thus, in case where the material is in contact with water, only a contact portion becomes gelatinized, so that water does not evenly permeate. This raises such problem

that it is impossible to realize high water absorbing rate (hereinafter, this problem is referred to as "fish eye").

In order to solve the disadvantage, there has been adopted a method in which each of the water absorbing materials is made into fine particles so that the surface area is increased so as to increase the water absorbing rate. In this case, the surface area of the water absorbing material increases, so that the water absorbing rate is increased to some extent, but a membrane occurs on the particle surface so as to be positioned in a portion which is in contact with water, so that the water does not evenly permeate. This does not result in improvement of the water absorbing rate.

The inventors of the present invention proposed an invention (Tokugansho 56-140571) in which: hydrophilic cross-linked polymer is dispersed in dispersion medium, and then a surface of the hydrophilic cross-linked polymer is cross-linked with a cross-linking agent. According to this method, in case where the water absorbing material is in contact with water, not only the contact portion is gelatinized and even permeation of water is promoted, so that this method is effective in raising the water absorbing rate. However, even this method fails to realize sufficient improvement of the water absorbing rate. Moreover, this method is disadvantageous in terms of the cost.

While, the inventors proposed an invention

(Tokugansho 59-181682) in which water-insoluble water absorbent resin and inorganic particles are blended with each other. This method is advantageous to some extent in raising the water absorbing rate but fails to realize sufficient improvement.

[PROBLEMS TO BE SOLVED BY THE INVENTION]

The inventors diligently studied so as to solve the problem which cannot be sufficiently solved by the conventional techniques in raising the water absorbing rate of the water absorbing material, that is, so as to solve the fish eye. As a result of the diligent study, they found that: a small amount of water containing polyvalent metal salt and/or hydroxide is added to polymer particles, and a surface of the polymer particles is cross-linked, so that absorbed liquid smoothly passes through the polymer particles without adhering to the polymer particles. As a result, they completed the present invention.

[MEANS TO SOLVE THE PROBLEMS]

The present invention relates to (i) a reformed water-insoluble water absorbent resin composition obtained by adding, as an essential component, water containing polyvalent metal salt and/or hydroxide to water-insoluble hydrophilic polymer particles made of hydrophilic and/or water-soluble monomer (first invention), (ii) a production method thereof (second invention), and (iii) a water absorbing and water retaining

agent (third invention).

As to the polyvalent metal salt or hydroxide used in the present invention, examples of polyvalent metal include: bivalent metal such as Mg, Ca, Ba, Zn, Fe, and trivalent metal such as Al and Fe; inorganic normal salt and double salt, such as halide thereof, nitrate, phosphate, sulfate, and carbonate, or low organic acid chloride such as oxalate and acetate, and hydroxide. Specific examples of the compound include calcium chloride, magnesium chloride, ferrous chloride, aluminum chloride, polychlorinated aluminum, iron chloride, iron nitrate, calcium nitrate, aluminum nitrate, magnesium phosphate, calcium phosphate, aluminum phosphate, magnesium sulfate, iron sulfate, aluminum sulfate, aluminum potassium sulfate, aluminum ammonium sulfate, calcium carbonate, magnesium carbonate, magnesium calcium carbonate, magnesium oxalate, calcium oxalate, magnesium acetate, calcium acetate, aluminum acetate, calcium hydroxide, and aluminum hydroxide. These compounds may be independently used, or a suitable combination thereof may be used. Among them, it is preferable to use a water-insoluble compound, and specific examples thereof include calcium chloride, magnesium chloride, ferrous chloride, aluminum chloride, polychlorinated aluminum, iron chloride, iron nitrate, calcium nitrate, aluminum nitrate, magnesium sulfate,

ferrous sulfate, aluminum sulfate, aluminum potassium sulfate, aluminum ammonium sulfate, magnesium acetate, calcium acetate, aluminum acetate, and calcium lactate. Among them, it is preferable to use calcium salt and aluminum salt, and it is particularly preferable to use sulfate and acetate as salt.

Examples of water used in the present invention include tap water, industrial water, groundwater, ion-exchange water, and pure water. It is preferable to use tap water.

Each water may be used in combination with hydrophilic organic solvent such as alcohol containing 1 to 4 carbon atoms (methyl alcohol, ethyl alcohol, isopropyl alcohol, and the like), ketone (acetone and the like), amide (N,N-dimethyl formamide and the like), and sulfoxide (dimethyl sulfoxide). A ratio at which water and these materials are combined is not particularly limited, but it is general that an amount of these materials is 100 times as large as one part of water.

Examples of the water-insoluble hydrophilic polymer made of hydrophilic and/or water-soluble monomer used in the present invention include: a polymer obtained by copolymerizing a material (A) such as (a hydrophilic and/or water-insoluble monomer) and/or (monomer which is changed into hydrophilic and/or water-soluble monomer by hydrolysis) and polysaccharide (B) (for

example, hydrolyzed starch-acrylnitrilgraft copolymer, cellulose-acrylic acid graft copolymer and salt thereof); a copolymer obtained by copolymerizing the material (A) and a cross-linking agent (C) (for example, a polyacrylamide cross-linked with divinyl compound (methylene bis acrylamide and the like) and partially hydrolyzed polyacrylamide, a cross-linked poval, a saponified vinylester-unsaturated carboxylic acid copolymer recited in Tokukaisho 52-14689 and Tokukaisho 52-27455, cross-linked polyethyleneoxide); a polymer obtained by polymerizing the material (A), the polysaccharide (B), and the cross-linking agent (C) as essential components and by carrying out hydrolysis as required (for example, cross-linked starch-acrylamide graft copolymer, cross-linked starch-acrylic acid graft copolymer and salt thereof which are recited in Tokukosho 53-46199 and Tokukosho 53-46200. Two or more kinds of these hydrophilic cross-linked polymers may be used together.

The thus obtained polymer particles are ordinarily in a dried powder state. It is preferable that a water content thereof is 20 wt% or less.

A particle size of the polymer particles is ordinarily 5 to 5000 μ or less, preferably 20 to 500 μ .

The polymer particles ordinarily have a water absorbing ability of 60 ml/g or more.

An amount of water newly used with respect to the

polymer particles ordinarily ranges from 0.005 to 50 wt%, preferably from 0.01 to 20 wt%, more preferably from 0.5 to 10 wt%. When the amount of water is less than 0.005 wt%, the surface of the polymer particles is not sufficiently reformed. When the amount of water exceeds 50 wt%, it is necessary to carry out the heat treatment and a surface layer of the polymer particles has an excessively high density, so that the water absorbing rate drops.

With respect to an amount of the hydrophilic cross-linking polymer, an amount of polyvalent metal salt which is soluble in water serving as the cross-linking agent ordinarily ranges from 0 to 1.0 wt%, preferably from 0.1 to 5 wt%. When the amount of the polyvalent metal salt is larger than 10 wt%, the water absorbing rate can be raised but the water absorbing ability significantly drops, so that it is difficult to practically use this as a water absorbent resin.

Examples of a method for adding water containing water-soluble polyvalent metal salt (hereinafter, water is used unless particularly mentioned) to the polymer particles are as follows: (i) Water is sprayed to the water-insoluble hydrophilic polymer particles so as to carry out contact treatment; (ii) the polymer particles are placed in water so as to be evenly mixed and the resultant is kneaded so as to carry out contact treatment.

A temperature in the contact treatment may be room temperature, so that it is not necessary to heat. However, heat treatment may be carried out, and heating time ranges from 1 to 120 minutes, preferably from 2 to 30 minutes. The resultant can be used without any modification after carrying out the contact treatment, but the resultant may be further dried.

In the reformed water absorbent resin composition of the present invention, an extender, a colorant, an ultraviolet absorbing agent, an oxidation inhibitor, a fungicide, a bactericide, a herbicide, a fertilizer, a perfumery, a deodorant, a reducer, and the like may be included. Particularly, in case where the reducer is included in the resin composition of the present invention, the metal salt used in the present invention serves as primary salt, so that the resin composition is additionally characterized in that the primary salt exhibits a deodorant ability.

Examples of the reducer include thiourea, L-ascorbic acid, and the like.

The water-insoluble water absorbent resin composition of the present invention can be used as a water absorbing and water retaining agent. Examples of the water absorbing and water retaining agent are as follows:

(i) Water absorbing and water retaining agent for water

absorbing article

A disposable diaper, a sanitary napkin, a wound dressing, an incontinence pad, a paper and fiber product water-absorbing-ability improving agent, a sweat-absorbency providing agent, and the like which are described in Tokugansho 49-149090 and Tokugansho 57-82566 for example.

(ii) Agroforestry/horticulture water retaining agent

A soil water retention improving agent, an agrochemical/fertilizer effect keeping agent, a bog moss alternative, a transplantation water retaining agent, a plant growing pot water retaining agent, and the like which are described in Tokukosho 55-4462, Tokokaisho 52-82715, Tokukosho 56-45882, Tokukaisho 58-31919, and the like for example.

(iii) Architectural water absorbing material

Interior architectural material anti-condensation materials such as a wall material, a ceiling material, and the like which are described in Tokukaisho 58-65075 and the like for example.

(iv) Other materials

A civil engineering and industrial dehydrating agent (agent dehydrating liquid such as methanol, ethanol, benzine, petroleum ether, gasoline, vegetable oil, and fuel oil), a heavy metal adsorbing agent, a sludge coagulating agent, agent for controlling/releasing various kinds of

chemicals, aroma chemicals, and the like, which are described in Tokukosho 58-1624, Tokukaisho 53-107430, and the like for example.

[Examples]

Each of the following examples further explains the present invention, but the present invention is not limited to them.

Examples 1 to 4

40 g of water-insoluble hydrophilic polymer particles (Sanwet IM-1000U (Sanyo Chemical Industries, Ltd.) containing about 15% fine particles of 50 μ or less) were placed into a chamber (1.8 litter) of a device having an air duct, an exhaust thereof, and a water spray nozzle (for example, a spray drying device CA-21 (Yamato Scientific Co., Ltd.), and water in which 10% of aluminum sulfate had been dissolved was sprayed to the polymer particles so that 0.1% of the water, 1% of the water, 5% of the water, and 10% of the water were respectively sprayed while bringing air into the chamber at 0.2 m²/minute, thereby obtaining water absorbent resin compositions [A], [B], [C], and [D].

Examples 5 to 8

In Examples 5 to 8, the same operation was carried out as Examples 1 to 4 except that: in bringing water in which 10% of aluminum sulfate had been dissolved was sprayed into the chamber, air brought into the chamber

was heated to 80°C and no treatment was performed during 5 minutes after bringing the air into the chamber, thereby obtaining water absorbent resin compositions [E], [F], [G], and [H].

Example 9

An amount of 0.9% saline absorbed in each of the water absorbent resin compositions obtained in Examples 1 to 8 and an absorbing rate thereof were measured. Results of the measurement are illustrated in Table 1. Note that, the amount of the absorbed saline was measured as follows. A bag made of nylon nonwoven cloth (200 mesh) was prepared, and 1 g of the resin composition was enclosed in the bag, and the bag was soaked in 0.9% saline for 30 minutes. After retrieving and draining the bag for 15 minutes, an increased weight was measured. Further, the absorbing rate was measured as follows. A nylon nonwoven cloth (200 mesh) was placed on a support board having small holes. On the nylon nonwoven cloth, 0.1 g of the resin composition was placed, and an undersurface thereof was brought into contact with the liquid, and an amount of 0.9% saline absorbed in the resin composition in 2 minutes was measured. The thus measured value was converted into an absorption amount per 1 g of the resin composition.

Comparative Examples 1 to 3

Comparative Example 1:

A product obtained without treating Sanwet IM-1000U was used.

Comparative Example 2:

The same operation as Example 1 was carried out except that aluminum hydroxide was mixed with Sanwet IM-1000U, thereby obtaining a water absorbent resin composition [J].

Comparative Example 3

The same operation as Example 3 was carried out except that only water was sprayed without mixing aluminum hydroxide with Sanwet IM-1000U, thereby obtaining a water absorbent resin composition [K].

Table 1

	Aluminum Hydroxide (wt%)	Water (wt%)	Aluminum Sulfate (wt%)	Absorption Amount (g/g)	Absorbing Rate (ml/g)
Example 1	—	0.1	0.01	64	33
Example 2	—	1.0	0.1	68	42
Example 3	—	5.0	0.5	73	53
Example 4	—	10.0	1.0	70	60
Example 5	—	0.09	0.01	65	49
Example 6	—	0.9	0.1	73	59
Example 7	—	4.5	0.5	78	62
Example 8	—	9.0	1.0	75	65
Comparative Example 1	—	—	—	50	10
Comparative Example 2	1.0	—	—	50	10
Comparative Example 3	—	5.0	—	50	11

[EFFECTS OF THE INVENTION]

The present invention relates to a water absorbent resin composition and a water absorbing and water retaining agent including the water absorbent resin composition, wherein even permeation of water is promoted and high water absorbing rate is realized. Each of the products of the present invention has the following characteristics: Not only the high water absorbing rate but also stability with respect to humidity is realized. That is, even when the water absorbent resin composition is left in high humidity, a blocking phenomenon hardly occurs between resin particles. Also, the product of the present invention is superior in stability through days, that is, superior in water retention and shape retention through extended period of time. Further, the product generates less dusts at the time of treatment of particles.

⑩ 日本国特許庁(JP)

⑪ 特許出願公開

⑫ 公開特許公報(A) 昭62-7745

⑬ Int. Cl.

C 08 K 3/10

識別記号

CAM

庁内整理番号

6845-4J

⑭ 公開 昭和62年(1987)1月14日

Jan. 14, 1987

審査請求 未請求 発明の数 3 (全5頁)

⑮ 発明の名称 吸水性樹脂組成物、その製法および吸水、保水剤

⑯ 特 願 昭60-147305

⑰ 出 願 昭60(1985)7月3日

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明 細 書

1. 発明の名称

吸水性樹脂組成物、その製法および吸水、保水剤

2. 特許請求の範囲

1. 親水性および/または水溶性単量体からの水不溶性、親水性重合体粒子に、必須成分として、多価金属の塩および/または水酸化物を含む水を付与させてなることを特徴とする改質された水不溶性吸水性樹脂組成物。

2. 多価金属の塩および/または水酸化物の量が該重合体成分に対して0.01~10重量%である特許請求の範囲第1項記載の吸水性樹脂組成物。

3. 水不溶性、親水性重合体がデンプン-アクリロニトリルグラフト共重合体の加水分解物、セルロース-アクリル酸グラフト共重合体およびその塩、ジビニル化合物で架橋されたポリアクリルアミドおよびその部分加水分解物、架橋ポバール、ビニルエステル-不飽和カルボン酸共重合体ケン化物、架橋ポリエチレンオキシド、架橋されたデ

ンプン-アクリルアミドグラフト共重合体ならびに架橋されたデンプン-アクリル酸グラフト共重合体およびその塩からなる群より選ばれる重合体である特許請求の範囲第1項または第2項記載の吸水性樹脂組成物。

4. 水不溶性、親水性重合体が(親水性および/または水溶性単量体)および/または(加水分解により親水性および/または水溶性単量体となる単量体)(A)と多糖類(B)との重合体;(A)と架橋剤(C)との重合体;または(A)と(B)と(C)とを必須成分として重合させ必要により加水分解を行うことにより得られる重合体である特許請求の範囲第1項ないし第3項のいずれか一項に記載の吸水性樹脂組成物。

5. 親水性および/または水溶性単量体からの水不溶性、親水性重合体を水分20重量%以下の粉末状樹脂粒子とし、多価金属の塩および/または水酸化物を含む水を該樹脂粒子に対し、0.01~20重量%となる量該樹脂粒子表面に散布する水不溶性吸水性樹脂の製造法。

特開昭62-7745(2)

6. 樹脂粒子が60ml/g以上の吸水力を有する高吸水性樹脂の粒子である特許請求の範囲第5項記載の製造法。

7. 多価金属の塩および/または水酸化物の量が該樹脂粒子に対して0.005～10重量%である特許請求の範囲第5あるいは6項に記載の製造法。

8. 親水性および/または水溶性単量体からの水不溶性、親水性重合体粒子に、必須成分として、多価金属の塩および/または水酸化物を含む水を付与させてなる水不溶性吸水性樹脂組成物を含有してなる吸水、保水剤。

9. 吸水、保水剤が吸収性物品用吸水、保水剤である特許請求の範囲第8項記載の吸水、保水剤。

10. 吸収性物品が使い捨ておむつ、生理用ナプキン、創傷包帯、失禁用パッド、各種紙および繊維製品用吸水性向上剤または吸汗性付与剤である特許請求の範囲第8項記載の吸水、保水剤。

11. 吸水、保水剤が農林、園芸用保水剤、建築用吸水材、土木および諸工業用脱水剤、重金属吸着剤、汚泥凝固剤または薬剤、香料のコントロール・

この欠点を改良するため、これらの吸水材料を微粉化して表面積を増大させ、水との接触面をふやすことで吸水速度を高める方法がとられてきた。この場合、吸水性材料の表面積がふえることから幾分吸水速度は速くなるが、粒子表面において水の接触部に皮膜を生じ均一な水の浸透が行なわれないため、吸水速度の改良にはつながらなかった。

本発明者等は特願昭56-140571号において親水性架橋重合体を分散媒に分散させた後、さらに架橋剤を該親水性架橋重合体の表面に架橋させることを提案した。この方法は吸水材料が水と接触した場合、接触部分だけでゲル化することなく、水の均一な浸透を促進するため、吸水速度を高めるために有効であるが、この方法によっても吸水速度の改良は、まだ十分満足できるものでなく、かつ非経済的な方法であつた。

一方、特願昭59-181682号においては水不溶性吸水樹脂と無機粒子とを混合することを提案しているが、この方法は吸水速度の向上に若干の効果はあるもののとても満足できるものではなかつ

た。リリース化剤である特許請求の範囲第8項記載の吸水、保水剤。

3. 発明の詳細な説明

〔産業上の利用分野〕

本発明は吸水性樹脂組成物、その製法および吸水、保水剤に関する。

〔従来の技術〕

近年、生理用品、紙おむつなどに架橋ポリエチレンオキシド、架橋ポバール、デンプンポリアクリロニトリルグラフト重合体の加水分解物、自己架橋型ポリアクリル酸金属塩など比較的高い吸水能力を有する吸水材料が出現し始めた。しかしながら、これら材料は吸水能力を有するものの高い吸水速度を必要とする生理用品、紙おむつなどに使用するには十分満足すべきものではなかつた。すなわち吸水能力を高めれば高めるほど、水との親和力が強まるため、これらの材料が水と接触した場合接触部分だけでゲル化を生じ水の均一な浸透がさまたげられ速やかな吸水速度が得られないという問題（以下ママコという）があつた。

た。

〔発明が解決しようとする問題点〕

本発明者らは吸水材料の吸水速度向上のためには従来の技術によつても十分解決され得ない問題点すなわちママコの解消を目的として鋭意研究を重ねた結果、重合体粒子に少量の多価金属の塩および/または水酸化物を含む水を与え重合体粒子の表面をさらに架橋することにより、被吸収液が重合体粒子間の付着なしに各重合体粒子間を容易に通過出来ることを発見し本発明に到つた。

〔問題を解決するための手段〕

本発明は親水性および/または水溶性単量体からの水不溶性、親水性重合体粒子に、必須成分として多価金属の塩および/または水酸化物を含む水を付与させることを特徴とする改質された水不溶性吸水性樹脂組成物（第一発明）、その製造方法（第二発明）およびその吸水、保水剤としての用途（第三発明）である。

本発明において用いられる多価金属の塩または水酸化物は、多価金属としてMg, Ca, Ba, Zn, Fe

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などの二価金属およびAl, Feなどの三価金属など；これら金属のハロゲン化物、硝酸塩、リン酸塩、硫酸塩、炭酸塩などの無機の正塩および複塩または修酸塩、酯酸塩などの低級有機酸塩など、および水酸化物であり；具体的な化合物としては塩化カルシウム、塩化マグネシウム、塩化第1鉄、塩化アルミニウム、ポリ塩化アルミニウム、塩化第2鉄、硝酸鉄、硝酸カルシウム、硝酸アルミニウム、リン酸マグネシウム、リン酸カルシウム、リン酸アルミニウム、硫酸マグネシウム、硫酸第1鉄、硫酸アルミニウム、硫酸アルミニウムカリウム、硫酸アルミニウムアンモニウム、炭酸カルシウム、炭酸マグネシウム、炭酸マグネシウムカルシウム、修酸マグネシウム、修酸カルシウム、酯酸マグネシウム、酯酸カルシウム、酯酸アルミニウム、水酸化カルシウム、水酸化アルミニウムなどがあげられる。これら化合物は単独であるいは併用して用いても良い。これらのうち好ましいものは水に可溶な化合物であり；具体的な化合物としては塩化カルシウム、塩化マグネシウム、塩化

第1鉄、塩化アルミニウム、ポリ塩化アルミニウム、塩化第2鉄、硝酸鉄、硝酸カルシウム、硝酸アルミニウム、硫酸マグネシウム、硫酸第1鉄、硫酸アルミニウム、硫酸アルミニウムカリウム、硫酸アルミニウムアンモニウム、酯酸マグネシウム、酯酸カルシウム、酯酸アルミニウム、~~修酸~~炭酸カルシウムなどがあげられる。これらのうち好ましいものはカルシウム塩、アルミニウム塩であり特に好ましい塩としては硫酸塩、酯酸塩である。

本発明において使用される水としては水道水、工業用水、地下水、イオン交換水、純水などがあげられる。好ましくは水道水である。

これらの水にはさらに親水性有機溶媒、例えば炭素数1~4のアルコール（メチルアルコール、エチルアルコール、イソプロピルアルコールなど）、ケトン（アセトンなど）、アミド（N, N-ジメチルホルムアミドなど）、スルホキシド（ジメチルスルホキシドなど）と併用してもよい。水とこれらの使用割合は特に限定されないが通常水1部に対し100倍程度までである。

本発明で使用される親水性および／または水溶性単量体からの水不溶性、親水性重合体としては（親水性および／または水溶性単量体）および／または（加水分解により親水性および／または水溶性となる単量体）(A)と多糖類(B)との重合体たとえばデンプン-アクリロニトリルグラフト共重合体の加水分解物、セルロース-アクリル酸グラフト共重合体およびその塩など；(A)と架橋剤(C)との重合体たとえばジビニル化合物（メチレンビスアクリルアミドなど）で架橋されたポリアクリルアミドおよびその部分加水分解物、架橋ポパー、特開昭52-14689号、特開昭52-27455号記載の架橋されたビニルエステル-不飽和カルボン酸共重合体ケン化物、架橋ポリエチレンオキシドなど；(A)と(B)と(C)とを必須成分として重合させ必要により加水分解を行うことにより得られる重合体たとえば特公昭53-46199号、特公昭53-46200号および特公昭55-4462号記載の架橋されたデンプン-アクリルアミドグラフト共重合体、架橋されたデンプン-アクリル酸グラフト共重合体およ

びその塩などがあげられる。これらの親水性架橋重合体は二種以上併用してもよい。

このようにして得られた重合体粒子は通常乾燥された粉末状であり水分は好ましくは20重量%以下のものである。

重合体粒子の粒度は通常5~5000 μ 以下、好ましくは20~500 μ である。

重合体粒子は通常60ml/g以上の吸水力を有するものである。

重合体粒子に対する新たに使用する水の量は通常0.005ないし50重量%、好ましくは0.01~20%、さらに好ましくは0.5~10%である。水の量が0.005%未満では重合体粒子の表面の改質が不十分であり、50%を越えると加熱処理が必要となるとともに重合体粒子の表面の密度が高くなり過ぎ、かえって吸収速度が低下する。

架橋剤としての水に可溶な多価金属の塩の使用量は、親水性架橋重合体に対して通常0~10重量%、好ましくは0.1~5重量%であり、10重量%より大きいと吸水速度の改良はできるものの吸水能

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力の低下がいちちるしくなり、吸水性樹脂として実用上使用し難い。

水に可溶な多価金属塩を含む水（以下断わらない限り水で代表させる）を重合体粒子に付与する方法としては(I)水不溶性、親水性重合粒子に水をスプレーし接触処理を行なわせる、(II)水に重合体粒子を投入し均一になるよう混練し接触処理を行う方法があげられる。

接触処理における温度は室温でよく特に加熱の必要はないが、加熱を行つてもよく時間は1~120分、好ましくは2~30分である。接触処理後はそのまま使用できるが、さらに乾燥させてもよい。

本発明の改良された吸水性樹脂組成物には増量剤、顔料、紫外線吸収剤、酸化防止剤、防カビ剤、殺菌剤、除草剤、肥料、香料、消臭剤、還元剤などを含有させて用いてもよい。とくに還元剤を本発明の樹脂組成物に含有させた場合は、本発明においても使用される金属塩が第一塩となり、この第一塩が脱臭能力を発現するという特徴が加わる。

例えば還元剤としてはチオ尿素、L-アスコル

ノール、ベンジン、石油エーテル、ガソリン、植物油、重油などの液状物の脱水剤など）、重金属吸着剤、汚泥凝固剤、各種薬剤、香料等のコントロール・リリース化剤などで、例えば特公昭58-1624号、特開昭58-107430等に記述されているもの。

〔実施例〕

以下、実施例により本発明をさらに説明するが、本発明はこれに限定されるものではない。

実施例1~4

水不溶性、親水性重合体粒子（三洋化成工業社製 サンウエット 1M-1000U；50μ以下の微粒子約15%含有）40gを空気の吹き込み口およびその排気口を開え、かつ水のスプレーノズルを備えた装置（例えば、ヤマト科学株式会社製噴霧乾燥装置 CA-21）のチャンバー（18ℓ）内に入れ、風量0.2m³/分で空気を吹き込みながら、重合体粒子に、硫酸アルミニウム10%を溶解させた水をそれぞれ0.1%、1%、5%、10%噴霧し、吸水性樹脂組成物(A)、(B)、(C)、(D)を得た。

ビン酸などが挙げられる。

本発明の水不溶性吸水性樹脂組成物は吸水、保水剤として使用できる。この吸水、保水剤としては下記があげられる。

(I) 吸水性物品用吸水、保水剤

使い捨ておむつ、生理用ナプキン、創傷包帯、失禁パット、各種紙および繊維製品用吸水性向上剤、吸汗性付与剤など、例えば特願昭49-149090号、特開昭57-82566号等に記述されているもの。

(II) 農林園芸用保水材

土壌保水性向上剤、農薬・肥料用効力持続剤、水石代替品、植物移植用保水剤、植物育成用ポット用保水剤など、例えば特公昭55-4462号、特開昭52-82715号、特公昭56-45882号、特開昭58-31919号等に記述されているもの。

(III) 建築用吸水材

壁材、天井材等の内装建材用結露防止剤など、例えば特開昭58-65075等に記述されているもの。

(IV) その他

土木および諸工業用脱水剤（メタノール、エタ

実施例5~8

実施例1~4において、チャンバー内で硫酸アルミニウム10%を溶解させた水を吹き込む際に、吹き込み空気を80℃に加熱し、吹き込み後5分間放置した性かは、同様の操作を行なつて、吸水性樹脂組成物(E)、(F)、(G)、(H)を得た。

実施例9

実施例1~8において得られた吸水性樹脂組成物の0.9%食塩水の吸収量および吸収速度を測定し、その結果を表-1に示した。なお吸収量の測定法は200メツシュのナイロン製不織布を袋状にし、これに樹脂組成物1gを封入して、30分間0.9%食塩水に浸漬した後、取り出して15分間水切りを行つた後増加重量を測定した。また吸収速度については小穴のあいた支持板の上に200メツシュのナイロン製不織布を置く。この上に0.1gの樹脂組成物を置き、下面より液体と接触させ2分間で樹脂組成物が0.9%食塩水を吸収する量を測定し、樹脂組成物1g当りの吸収量に換算した。

比較例1~8

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表 1

- 比較例1 サンウエット 1M-1000 U 無処理品。
- 比較例2 実施例1においてサンウエット 1M-1000 Uに水酸化アルミニウムを混合することによつて吸収性樹脂組成物〔J〕を得た。
- 比較例3 実施例3においてサンウエット 1M-1000 Uに水酸化アルミニウムを混合することなく水のみを噴霧することによつて吸収性樹脂組成物〔K〕を得た。

	水酸化 アルミニウム (重量%)	水分量 (重量%)	硫酸アルミ ニウム量 (重量%)	吸収量 (g/g)	吸収速度 (ml/g)
実施例1	—	0.1	0.01	64	38
2	—	1.0	0.1	68	42
3	—	5.0	0.5	73	58
4	—	10.0	1.0	70	60
5	—	0.09	0.01	65	49
6	—	0.9	0.1	78	59
7	—	4.5	0.5	78	62
8	—	9.0	1.0	75	65
比較例1	—	—	—	50	10
2	1.0	—	—	50	10
3	—	5.0	—	50	11

〔発明の効果〕

本発明の吸水性樹脂組成物およびこれを含有する吸水、保水剤は水の均一な浸透性を促進し著しく高い吸水速度を有する吸水性樹脂組成物である。本発明による製品の特徴は、前述の吸水速度の向上のほか、湿度に対する安定性、すなわち本発明の吸水性樹脂組成物を高湿度下に放置しても、樹

脂の粒子同志がブロッキング現象を起しにくいという特長、経日安定性、すなわち長期にわたる使用中の保水性、保形性維持の点でも優れている。更に粉体取扱い時の発塵発生が少ないという特長を有する。

特許出願人 三洋化成工業株式会社

